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An Improved Method For Preparing Gravimetric Standard Gas Mixtures of Helium-4 in Nitrogen

By Nabil A. Bibawy and David E. Emerson

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BUREAU OF MINES

UNITED STATES DEPARTMENT OF THE INTERIOR

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Manuel Lujan, Jr., Secretary

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T S Ary, Director

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mm Hg	millimeter of mercury
cm^3	cubic centimeter	mol pct	mole percent
g	gram	pct	percent
kg	kilogram	ppb	part per billion
L	liter	ppm	part per million
L/min	liter per minute	ppt	part per trillion
mg	milligram	psig	pound (force) per square inch, gauge
min	minute	RH	relative humidity
mL	milliliter		

AN IMPROVED METHOD FOR PREPARING GRAVIMETRIC STANDARD GAS MIXTURES OF HELIUM-4 IN NITROGEN

By Nabil A. Bibawy[1] and David E. Emerson[2]

ABSTRACT

An improved method for preparing gravimetric standard gas mixtures of helium-4 in nitrogen has been developed by the U.S. Bureau of Mines. A single-pan 12-kg analytical balance that has a sensitivity of 3 mg is used to prepare the mixture. The balance will accommodate a cylinder having a volume of approximately 4 L that weighs approximately 5 kg. The method has been improved to a precision of ±0.04 pct by performing four successive dilutions, by improved handling of gases in the manifold, and by using an improved analytical method to select high-purity gases.

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INTRODUCTION

This report describes the apparatus and technique developed by the U.S. Bureau of Mines to prepare accurate ppm-range gravimetric standard gas mixtures of helium-4 in nitrogen. These mixtures are used to provide calibration gases for determining helium-4 in natural gases, process gases, and research streams. The accuracy of the calibration standard being prepared has a direct bearing on the accuracy that can be achieved when using these mixtures for calibration of analytical instruments.

In 1965, Miller (*1*)[3] reported a method for preparing gravimetric standards utilizing a double-pan balance with a sensitivity of 0.012 g; precision was ±0.05 mol pct or better per component in a mixture in the percent range, and ±1 pct per component in the ppm range.

In 1985, Loya (*2*) reported a method for preparing ppt-range gravimetric standard gas mixtures with a relative error of less than 1 pct.

This method reduces contamination and handling errors and uses improved analytical methods to select high-purity gases for the mixtures to improve the precision of the standard to ±0.04 pct.

DESCRIPTION OF APPARATUS

The apparatus consists of a high-pressure stainless steel manifold, metering valves, pressure transducers, a pressure and vacuum vent system, a 650-L/min vacuum pump, a single-pan 12-kg balance with concomitant class M weights certified by the National Institute of Standards and Technology, and instruments for measuring atmospheric conditions.

A 12-kg Transmetrics[4] single-pan high-capacity balance with 3-mg sensitivity is utilized for all weighings. The single-pan balance determines the last milligram of each weighing by using a force balance transducer that restores the weight beam to a preset null position. The force required to null the beam is converted to the weight required to complete the determination. The readability of the balance is to the nearest 1 mg.

The manifold is shown in figure 1. High-purity nitrogen containing less than 5 ppb helium-4 is used. Cylinder *A* containing the diluent nitrogen and cylinder *B* containing a gravimetric mixture of solute helium are connected at valves *1* and *2*, respectively. Weighing cylinder *C* is connected at valve *4*. Cylinder *D*, which is used to obtain "blank" samples for determining the residual helium-4 content in the system, is connected at valve *7*. Sample cylinder *D* is a 500-cm^3 steel cylinder rated at 1,800 psig and is fitted with a stainless steel, O-ring-sealed stem, Kel-F-seat metering valve. Cylinder port connections *E* for valves *1*, *2*, *4*, and *7* are O-ring-sealed, zero-clearance, stainless steel couplings.

MANIFOLD PREPARATION

The manifold is vented by opening valve *5* to the atmosphere, closing it when the pressure transducer reads 50 psig, and then evacuating to less than 0.1 torr by opening valve *6*. A O-to 500-psig transducer is used to measure the gas pressure with an accuracy of ±0.05 pct full scale.

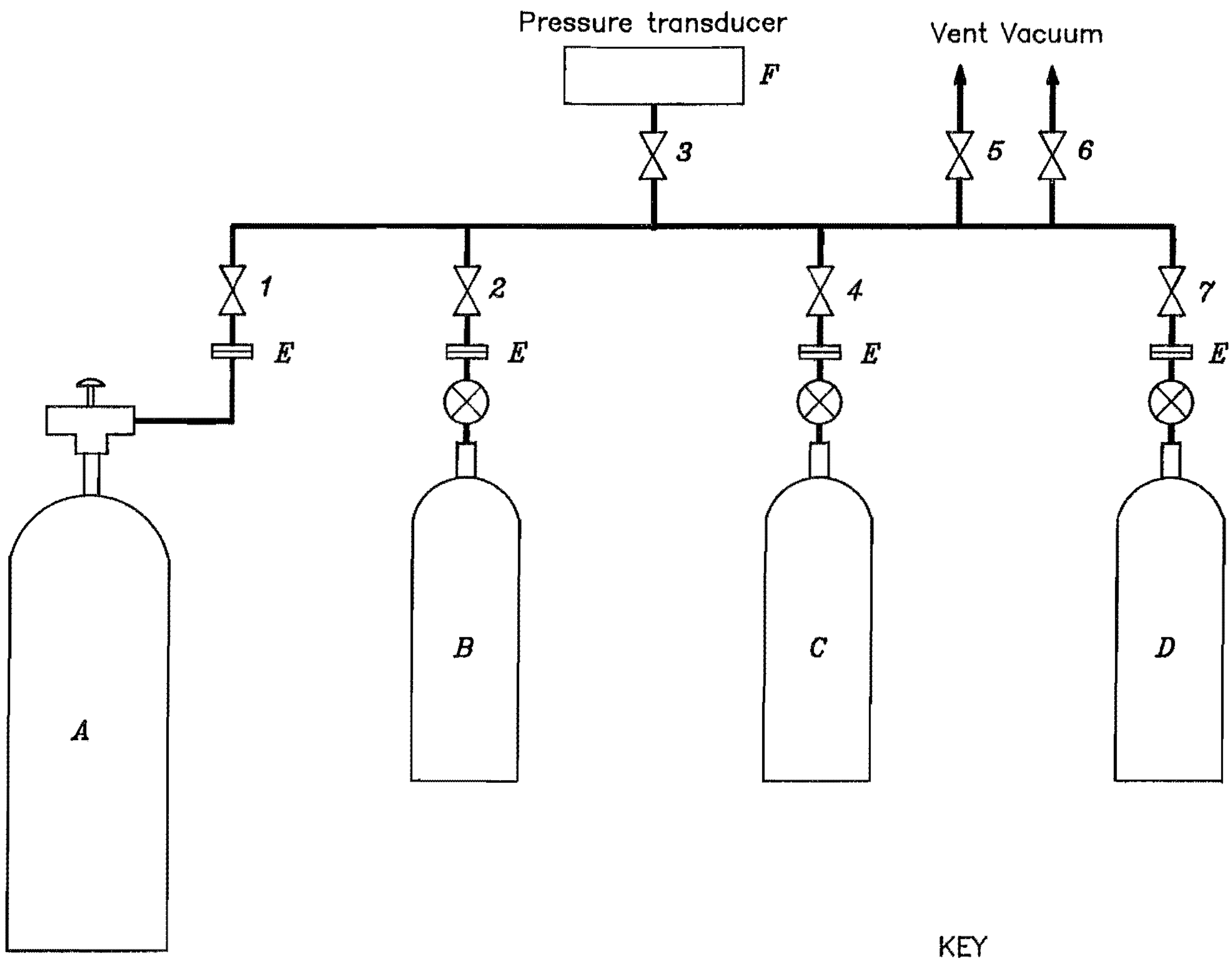
The technique to detect and remove contaminants involves purging the system with nitrogen containing less than 5 ppb helium-4 and collecting samples for analyses. The purge samples are analyzed using a helium-4 mass spectrometer described by Seitz (*3*). The manifold is filled with the nitrogen to 1,000 psig and left for 15 min before a "blank" sample is collected in cylinder *D* at 250 psig. When the "blank" sample's helium-4 content is within ±0.5 ppb of the helium-4 content of the purge nitrogen, the system is ready for use. If excess helium-4 is found, the system is again purged and checked for leaks, and the procedure is repeated until the ±0.5 ppb limit is reached.

CONTAINER PREPARATION

Prior to connecting a valve to weighing cylinder *C*, inspections are conducted to assure that components are free from corrosion, rated for the intended pressure, and constructed such that no weight loss due to handling occurs. After installing the valve, the cylinder is connected to the manifold, evacuated, filled with nitrogen to 1,800 psig, and soap-bubble-leak-tested at all connections. The cylinder is vented to the atmosphere and then degassed, using a previously described precedure (*4*).

[3]Italic numbers in parentheses refer to items in the list of references at the end of this report.

[4]Reference to specific products does not imply endorsement by the U.S. Bureau of Mines.



KEY

1–7	Metering valves
A	Diluent gas
B	Solute gas
C	Weighing cylinder
D	Blank samples
E	O–ring-sealed coupling
F	0- to 5,000–psig transducer

Figure 1.–Diagram of manifold used to prepare mixtures.

GAS ADDITION

To prepare a gas mixture of specified composition, the amount of each component to be added to the system is estimated. Dalton's law is used to calculate the required partial pressure of each component as follows:

$$M_t P_t = M_p P_p$$

and

$$P_t = \frac{M_p P_p}{M_t},$$

where P_t = the calculated partial pressure for each component, psig,

M_p = the desired mole fraction of the component in the mixture,

P_p = the total pressure of the mixture, psig,

and M_t = the mole fraction of the component before dilution.

P_t is the calculated partial pressure of the solute gas required to obtain the concentration in the new mixture. For example, to prepare a 1,000-psig (P_p) mixture of 48 ppm (M_p) helium-4 in nitrogen using a primary standard mixture containing 1,031.04 ppm (M_t) helium-4,

$$P_t = \frac{(48 \times 10^{-6})\ 1{,}000 \text{ psig}}{0.103104 \times 10^{-2}} = 46.55 \text{ psig.}$$

Therefore, 46.55 psig of solute gas containing 1,031.04 ppm helium-4 is required to make 1,000 psig of 48 ppm helium-4 in nitrogen. To prepare the mixture, cylinders *A, B, C,* and *D*, as shown in figure 1, are attached at valves *1, 2, 4,* and *7*, respectively. To evacuate the manifold, all valves are opened except valve *5*. After the manifold is evacuated, the valves for cylinders *C* and *D* are opened.

Vacuum valve *6* is then closed, and cylinders *C* and *D* are purged and evacuated by adding and removing 10 psig of the diluent nitrogen. A "blank" sample is taken at 250 psig and analyzed. When the helium-4 analysis is within ±0.5 ppb of the original helium-4 content, the system is ready to prepare the gravimetric standard.

A careful inspection of weighing cylinder *C* is repeated, and any debris that could fall off and result in a tare weight change is removed. Weighing cylinder *C* is then attached to the manifold. Cylinder *C* and valve *4* are opened, and the manifold and cylinder *C* are evacuated. Cylinder *C* is purged by opening and closing the vacuum valve, admitting 10 psig of solute gas, and evacuating again. The tare weight of cylinder *C* is determined, and the cylinder is reattached to the manifold. The manifold is purged again with solute gas and reevacuated. To prepare a mixture of 48 ppm helium-4 in nitrogen, the calculated solute pressure of 46.55 psig is added to cylinder *C* by opening cylinder valve *B* and observing the transducer indicator *F*. When 46.55 psig is reached, the valves of cylinders *B* and *C* are closed. The manifold is then evacuated, valves *2* and *4* and cylinder *C* are closed, and cylinder *C* is ready for the second weighing session. Subsequent to the second weighing session, the cylinder is attached to the manifold, valve *4* is opened, and the manifold is evacuated to the cylinder valve. The manifold is purged at least three times by admitting the diluent gas from cylinder *A* and evacuating the manifold. A second "blank" sample is obtained in cylinder *D* and analyzed for helium-4.

Prior to opening the cylinder *C* valve, the diluent is admitted to the manifold at a pressure at least twice the pressure in cylinder *C*. This pressure differential is maintained to guarantee that no flow out of cylinder *C* occurs. Cylinder *C* is opened, and the diluent is transferred from cylinder *A* until 1,000 psig is reached, as indicated on transducer indicator *F*. Valve *4* and cylinder *C* are then closed, and cylinder *C* is disconnected and weighed.

WEIGHING PROCEDURE

All weighings are made on a single-pan, substitution-type analytical balance of 12-kg capacity and 3-mg sensitivity. Prior to each weighing, the cylinder is allowed to equilibrate to the balance temperature. The balance weights have been calibrated against National Institute of Standards and Technology class M standard weights.

The cylinder is handled gently with a lintless cloth and placed on a clean surface between weighings. The data for preparing a standard are recorded as shown in table 1.

Table 1.–Mass and buoyancy determination data for each weighing

Session 1	Session 2	Session 3	Session 1	Session 2	Session 3
WEIGHT READINGS, g			BAROMETER TEMPERATURE READINGS, °C		
3,827.440	3,839.881	4,094.069	22.65	22.50	22.54
3,827.445	3,839.889	4,094.069	22.71	22.71	22.73
3,827.449	3,839.880	4,094.080	22.78	22.75	22.75
ZERO BALANCE READINGS, g			BAROMETRIC PRESSURE READINGS, mm Hg		
0.169	0.181	0.175	672.80	672.00	671.40
.173	.191	.177	672.80	672.00	671.40
.178	.194	.176	672.80	672.00	671.40
.180	.192	.179			
COUNTERBALANCE WEIGHT OF CYLINDER, g					
3,827	3,839	4,094			

Balance upper chamber relative humidity readings, session 1-3: 0.18
Balance lower chamber relative humidity readings, session 1-3: 0.26
Balance upper chamber temperature readings, sessions 1-3: 25 °C
Balance lower chamber temperature readings, sessions 1-3: 25 °C
Calculated displacement volume, sessions 1-3: 4,021 mL

CALCULATION

A computer program is used to calculate the composition of the gravimetrically prepared standard gas mixtures (*5*). In preparing a binary mixture, three weighing sessions are conducted consisting of three or more weighings each. The computer program is designed to accept up to 12 components.

BUOYANCY CORRECTION

To correct for buoyancy (*5*), the external volume of the weighing cylinder is determined by water displacement as shown in figure 2. Container *1* is filled to overflowing before the weighing cylinder is carefully lowered into the water. The water that is displaced is collected in container *2*. The displaced water is weighed, and the container's volume is calculated from water density tables. Other data required in calculation of the buoyancy correction are density of air in balance weighing chamber (upper chamber), density of air in balance weighing chamber (lower chamber), and volume of utilized weights. The data are obtained using a thermometer accurate to ±1 °C, direct-reading hygrometers accurate to ±0.03 RH, and a mercurial barometer accurate to ±0.05 mm Hg. These data are also given in table 1.

RESULTS

The composition of gases used to prepare the helium-in-nitrogen standard is shown in table 2. The resulting gravimetric standard mixture shown in table 3 was calculated to contain 48.067 ppm helium-4. This value is within 0.14 pct of the desired helium-4 content of 48 ppm.

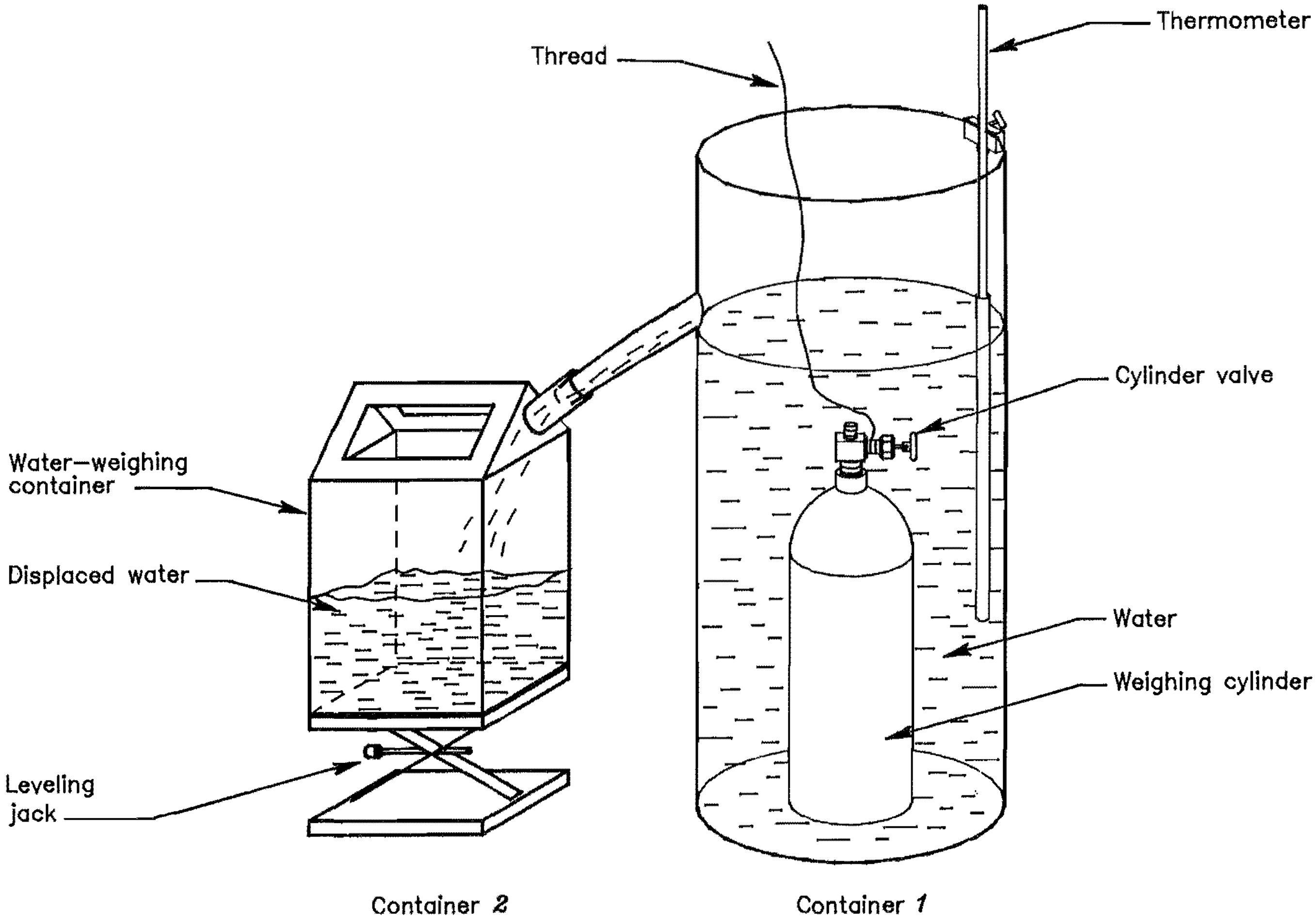


Figure 2.–Water displacement apparatus.

Table 2.–Composition of gases used to prepare weighed standard

	Gravimetric standard (S-417), cylinder B (*1*)		Nitrogen, cylinder A	
	Mole fraction	Standard error	Mole fraction	Standard error
He-4	0.00103104	0.000000304	0.0000000036 (*3*)	0.0000000005
H_2	.0000008	.0000008	.0000006	.0000001
N_e	<.0000008	.0000008	.000025	.000025
N_2	.998829	.000071	.999082	.000199
CH_4	.00000006	.00000005	.00000698	.00000005
O_2	.00006	.00005	.000046	.000002
Ar	.00004	.00004	.00008	.00002
CO_2	.000043	.000004	.000004	.000004

Table 3.–Weighed standard data

Component	Concentration	Standard error	Relative error, pct
He-4	48.067 ppm	0.019 ppm	0.04
N_2	99.986 pct	0.0051 pct	.005
CH_4	6.6 ppm	1.7 ppm	25.
O_2	7 ppm	2 ppm	35.
Ar	80 ppm	20 ppm	25.
CO_2	<4 ppm	-	-
Ne	<0.6 ppm	-	-
H_2	<0.6 ppm	-	-

CONCLUSIONS

A method has been developed for preparing ppm helium-4-in-nitrogen gravimetric standards with a precision of ±0.04 pct. The method minimizes cylinder tare weight changes, erroneous measurements, contamination, and calculation errors. The weighed standards can be prepared so that the calculated helium-4 content is within 0.14 pct of the desired helium-4 content.

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